

PAT Search

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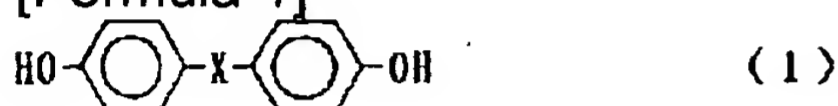
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## CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1)

[Formula 1]



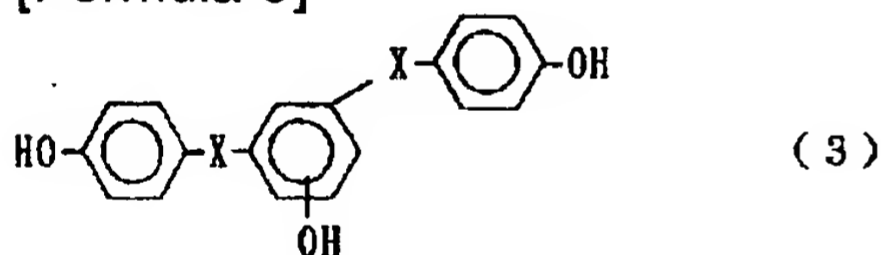
It is the following general formula (2) in 4 expressed with (however, the inside X of a formula is a divalent radical), and 4'-bisphenols.

[Formula 2]



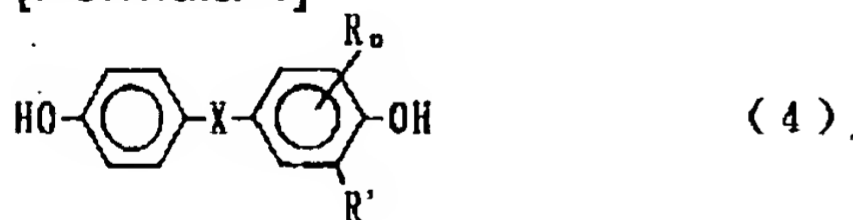
It is 2, the 4'-bisphenols, and the following general formula (3) which are expressed with (however, the inside X of a formula is a divalent radical).

[Formula 3]



They are the tris phenols expressed with (however, the inside X of a formula is a divalent radical), and the following general formula (4).

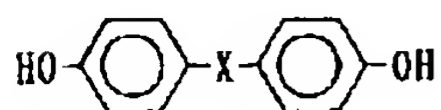
[Formula 4]



(-- however -- a formula -- inside -- X -- divalent -- a radical -- it is -- R -- and -- R -- ' -- a carbon number -- one -- more than -- an alkyl group -- it is -- n -- zero -- or -- one -- an integer -- it is --) -- expressing -- having -- alkylation -- four -- four -- ' - a bisphenol -- a kind -- from -- choosing -- having had -- at least -- one -- a sort -- phenolic -- a compound -- the sum total -- 50 - 10,000 -- weight -- ppm -- the range -- containing -- things -- the description -- \*\* -- carrying out -- a polymer -- a raw material -- \*\* -- a bisphenol -- a kind .

[Claim 2] The following general formula characterized by adding the bisphenols which have at least one substituent at least in orthochromatic to the hydroxyl group of 1, and do not have a substituent at least in orthochromatic to other hydroxyl groups in the range of the 50 - 10,000 weight ppm to 4 and 4'-bisphenols (1)

[Formula 5]



( 1 )

They are the bisphenols for polymer raw materials expressed with (however, the inside X of a formula is a divalent radical).

[Claim 3] It faces manufacturing the bisphenols for polymer raw materials according to claim 1. The general formula in 4 expressed with a general formula (1), and 4'-bisphenols (2), (3) The sum total content of the phenolic compound expressed with (4) is measured. And when the sum total content is lower than the 50 weight ppm \*\* [ whether it mixes with a phenolic compound (2), (3) and 4 with many sum total contents of (4), and 4'-bisphenols (1), and ] \*\* [ whether a by-product wit. many sum total contents of the phenolic compound (2) collected at the purification process at the time of manufacture of 4 and 4'-bisphenols (1), (3), and (4) is added, and ] Or at least one sort of compounds chosen from the phenolic compound (2) compounded according to \*\*, (3), and (4) are added. When there are more the sum total contents than the 10,000 weight ppm, [ \*\* and also ] [ whether it refines and ] Or it mixes with a \*\* phenolic compound (2), (3) and 4 with few sum total contents of (4), and 4'-bisphenols (1). The manufacture approach of the bisphenols for polymer raw materials characterized by adjusting the sum total content of the phenolic compound expressed with a general formula (2), (3), and (4) within the limits of the 50 - 10,000 weight ppm.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to 4 [ useful as a raw material for manufacture of various transparent polymers ], 4'-bisphenols, and the manufacture approach of those, and relates in more detail that the polymer manufactured as a raw material colors 4 and 4'-bisphenols to the bisphenols for polymer raw materials which can be prevented as much as possible, and the manufacture approach of those.

[0002]

[Description of the Prior Art] For example, generally, bisphenol A which is one of typical 4 and the 4'-bisphenols makes an acetone and a superfluous phenol react to the bottom of existence of an acid catalyst, after cooling this, depositing the crystal of the adducts of bisphenol A and a phenol, after removing water, an acetone, and/or a catalyst from the obtained reaction mixture, and separating this crystal from a mother liquor, carries out dephenolated processing and is manufactured.

[0003] And to excel in a hue, like for this bisphenol A not only to say that there are only few impurity contents, but when using as a manufacture raw material of transparent polymers, such as an application as which a high grade is required, for example, a polycarbonate, polyester, a polyether, and an epoxy resin, does not have coloring is also demanded.

[0004] For this reason, in order to manufacture bisphenol A which was excellent in the hue without coloring etc. in the former, How to decolorize by acid treatment, such as thioglycolic acid, to bisphenol A (JP,47-43937,B), How (JP,37-10788,B) to add and process a phosphoric-acid alkaline-earth-metal salt etc., How to recrystallize the adducts of bisphenol A and a phenol with water or an aromatic hydrocarbon solvent (JP,5-294871,A), In case a phenol is removed from the adducts of bisphenol A and a phenol by the centrifugal film evaporator, the approach (JP,5-294877,A) of maintaining this centrifugal film evaporator to a predetermined pressure, and washing with a phenol etc. is proposed.

[0005] However, even if it manufactured bisphenol A which was excellent in the hue which does not have coloring etc. at a high grade by such approach, when the severe transparent polymer of a demand is manufactured and fabricated about hues, such as a polycarbonate for optics, using this bisphenol A, the polymer which manufactured and was fabricated again may yellow by the heat history in that case.

[0006]

[Problem(s) to be Solved by the Invention] Then, this invention persons reached [ that the purpose can be attained and ] a header and this invention by making a predetermined phenolic compound exist at a predetermined rate in 4 which can prevent that coloring of yellowing etc. occurs at the time of polymer manufacture and its shaping as much as possible, and the result which examined - bisphenols and this 4 '4, 4'-bisphenols.

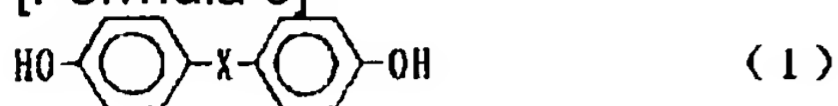
[0007] Therefore, the purpose of this invention is to offer the bisphenols for polymer raw

materials which can prevent that the polymer which was manufactured as a raw material and fabricated colors 4 and 4'-bisphenols as much as possible. Moreover, other purposes of this invention are to offer the approach of manufacturing such bisphenols for polymer raw materials.

[0008]

[Means for Solving the Problem] That is, this invention is the following general formula (1).

[Formula 6]



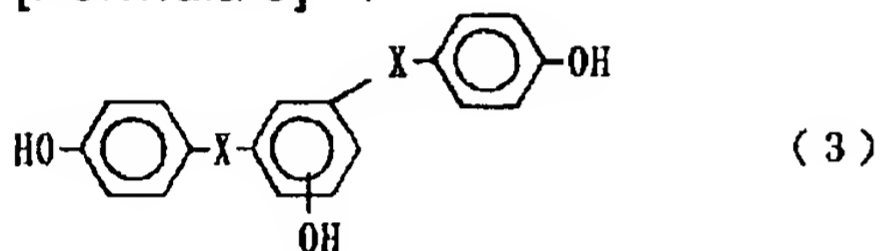
It is the following general formula (2) in 4 expressed with (however, the inside X of a formula is a divalent radical), and 4'-bisphenols.

[Formula 7]



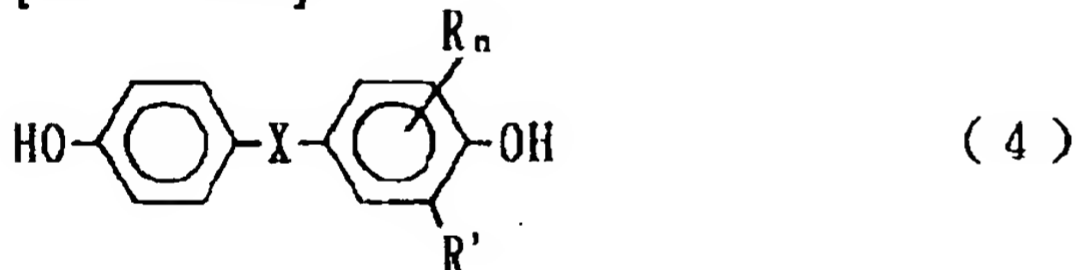
It is 2, the 4'-bisphenols, and the following general formula (3) which are expressed with (however, the inside X of a formula is a divalent radical).

[Formula 8]



They are the tris phenols expressed with (however, the inside X of a formula is a divalent radical), and the following general formula (4).

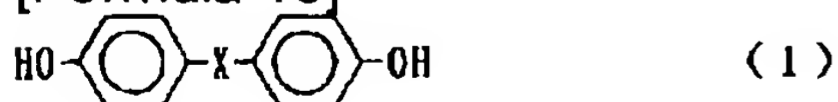
[Formula 9]



(-- however -- a formula -- inside -- X -- divalent -- a radical -- it is -- R -- and -- R -- ' -- a carbon number -- one -- more than -- an alkyl group -- it is -- n -- zero -- or -- one -- an integer -- it is --) -- expressing -- having -- a --ylation -- four -- four -- ' -- a bisphenol -- a kind -- from -- choosing -- having had -- at least -- one -- a sort -- phenolic -- a compound -- the sum total -- 50 - 10,000 -- weight -- ppm -- the range -- containing -- a polymer -- a raw material -- \*\* -- a bisphenol -- a kind -- it is .

[0009] Moreover, this invention is the following general formula (1) which added the bisphenols which have at least one substituent at least in orthochromatic to the hydroxyl group of 1, and do not have a substituent at least in orthochromatic to other hydroxyl groups in the range of the 50 - 10,000 weight ppm to 4 and 4'-bisphenols.

[Formula 10]



They are the bisphenols for polymer raw materials expressed with (however, the inside X of a formula is a divalent radical).

[0010] The general formula in 4 which faces manufacturing such bisphenols for polymer raw materials, and is expressed with a general formula (1), and 4'-bisphenols (2), (3) The sum total content of the phenolic compound expressed with (4) is measured. And when the sum total

content is lower than the 50 weight ppm \*\* [ whether it mixes with a phenolic compound (2), (3) and 4 with many sum total contents of (4), and 4'-bisphenols (1), and ] \*\* [ whether a by-product with many sum total contents of the phenolic compound (2) collected at the purification process at the time of manufacture of 4 and 4'-bisphenols (1), (3), and (4) is added, and ] Or at least one sort of compounds chosen from the phenolic compound (2) compounded according to \*\*, (3), and (4) are added. When there are more the sum total contents than the 10,000 weight ppm, [ \*\* and also ] [ whether it refines and ] Or it mixes with a \*\* phenolic compound (2), (3) and 4 with few sum total contents of (4), and 4'-bisphenols (1). It is the manufacture approach of the bisphenols for polymer raw materials which adjust the sum total content of the phenolic compound expressed with a general formula (2), (3), and (4) within the limits of the 50 - 10,000 weight ppm.

[0011] The above-mentioned general formula (1) in - (4) as a divalent radical X For example, -C(CH<sub>3</sub>)<sub>2</sub>-, -CH(CH<sub>3</sub>)-, -SO<sub>2</sub>-, -CH<sub>2</sub> C(CH<sub>3</sub>)<sub>2</sub>-, -O-, etc. can be mentioned, and it is desirable for the next door of the benzene ring to be that of a bulky potato like -C(CH<sub>3</sub>)<sub>2</sub>- or -SO<sub>2</sub>-.

[0012] Specifically in this invention, bisphenol A, Bisphenol F, bis(hydroxyphenyl) ethane, a dihydroxy biphenyl, bis(hydroxyphenyl) trimethylcyclohexane, bis(hydroxyphenyl) butane, bis(hydroxyphenyl) sulfide, a bis(hydroxyphenyl) sulfone, a bis(hydroxyphenyl) ketone, etc. can be mentioned as 4 expressed with a general formula (1), and 4'-bisphenols.

[0013] Moreover, as a phenolic compound made to exist in this 4 and 4'-bisphenols, they are any one or more sorts of 2 expressed with a general formula (2), and the 4' alkylation 4 and 4 expressed with tris phenols and general formula (4) which are expressed with - bisphenols and general formula (3)'-bisphenols. And although there is a phenolic compound expressed with the above-mentioned general formula (2) and a general formula (4) as "bisphenols which has at least one substituent at least in orthochromatic to the hydroxyl group of 1, and does not have a substituent at least in orthochromatic to other hydroxyl groups" added to this 4' and 4'-bisphenols, it is not limited to this. In addition, as a substituent which it has at least in orthochromatic, an alkyl group, an aryl group, etc. are raised, and also X in a general formula (1) is seen as this substituent.

[0014] As 2 expressed with a general formula (2), and 4'-bisphenols, there is a - bisphenol A, and 2 and 4' 2, 4'-bis(hydroxyphenyl) sulfone etc. In the case of such a compound, it is desirable that the divalent radical X which adjoins the OH radical of the 2nd place is that of a bulky potato.

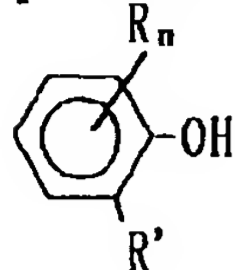
[0015] and a compound like 2 and 4'-bisphenol A -- 4 and 4' - the description by other amounts of impurities increasing to coincidence, although specified quantity content can be carried out by controlling extent of purification since it is obtained as a by-product at the time of manufacturing - bisphenol A etc. -- since aggravation arises, it is disadvantageous to reduce extent of purification in vain. Since filtrate and the fraction by which 2 and a compound like 4'-bisphenol A are discharged by high concentration as an impurity at purification processes, such as 4 and 4'-bisphenol A, exist, it is advantageous to refine these as occasion demands and to carry out specified quantity addition. Of course, it is also suitable to carry out specified quantity addition of a compound like 2 obtained separately and 4'-bisphenol A.

[0016] Moreover, there is a compound which a bisphenol, a phenol, and an acetone react and is obtained as tris phenols expressed with a general formula (3). And in the general formula of these tris phenols, the permutation location of an OH radical is the 2nd place or the 4th place. Since such tris phenols are also obtained as a by-product at the time of manufacturing 4 and 4'-bisphenol A etc., they are good to carry out specified quantity addition like the above.

[0017] Furthermore, since the phenolic compound expressed with a general formula (4) is obtained as a by-product as well as [ in 4 and 4'-bisphenols ] the above, it is good to carry out specified quantity addition like the above. Moreover, as an approach in which this is made to

exist positively, it is the following general formula (5) as some phenol raw materials at the time of manufacture of 4 and 4'-bisphenols.

[Formula 11]



( 5 )

The specified quantity of alkylphenol expressed with (however, the inside R of a formula and R' are with a carbon numbers of one or more alkyl groups, and n is the integer of 0 or 1) may be added.

[0018] As this alkylphenol, 2-tertiarybutyl phenol, 2-tertiarybutyl-6-methyl phenol, 2, 6-di-tertiary-butyl phenol, o-cresol, o-ethylphenol, 2, and 6-xilenol etc. can be mentioned typically. moreover, about the rate which adds such alkylphenol For example, if it adds 1% of the weight in a phenol raw material, since the phenolic compound of a general formula (4) will generate at about 1% of the weight of a rate in 4 manufactured and 4'-bisphenols You may add so that this phenolic compound may generate within the limits of the 50 - 10,000 weight ppm in 4 and 4'-bisphenols. Moreover, it adds for the business which the phenolic compound of a general formula (4) generates exceeding the 10,000 weight ppm, for example in 4 and 4'-bisphenols. 4 obtained and 4'-bisphenols are mixed with 4 of a high grade, and 4'-bisphenols, and you may make it adjust the sum total content of a phenolic compound within the limits of the 50 - 10,000 weight ppm.

[0019] As a rate of making the phenolic compound expressed with the above-mentioned general formula (2), (3), and (4) existing in 4 and 4'-bisphenols Usually, 50-10,000 ppm is 200-3000 ppm preferably. Coloring of yellowing etc. may occur in the polymer which was manufactured using such 4 and 4'-bisphenols and was fabricated when fewer than 50 ppm, and on the contrary, when it increases more than 10,000 ppm, there are 4 and a possibility that 4'-bisphenols itself may color.

[0020] And as an approach of making these phenolic compound existing in 4 and 4'-bisphenols, although there is especially no limit, it is good to carry out by the following approaches preferably.

[0021] That is, the sum total content of the phenolic compound first expressed with the general formula (2) in 4 expressed with a general formula (1) and 4'-bisphenols, (3), and (4) is measured.

[0022] and when the measured sum total content is lower than the 50 weight ppm \*\* [ whether it mixes with a phenolic compound (2), (3) and 4 with many sum total contents of (4), and 4'-bisphenols (1), and ] \*\* [ whether a by-product with many sum total contents of the phenolic compound (2) collected at the purification process at the time of manufacture of 4 and 4'-bisphenols (1), (3), and (4) is added, and ] Or at least one sort of compounds chosen from the phenolic compound (2) compounded according to \*\*, (3), and (4) are added, and the sum total content of the phenolic compound expressed with a general formula (2), (3), and (4) is adjusted within the limits of the 50 - 10,000 weight ppm. Moreover, it is also the same as when adding the above "the bisphenols which have at least one substituent at least in orthochromatic to the hydroxyl group of 1, and do not have a substituent at least in orthochromatic to other hydroxyl groups."

[0023] Moreover, when there are more measured sum total contents than the 10,000 weight ppm, \*\* and also the sum total content of a phenolic compound which refines, or is mixed with \*\* phenolic compound (2), (3) and 4 with few sum total contents of (4), and 4'-bisphenols (1), and is expressed with a general formula (2), (3), and (4) are adjusted within the limits of the 50 - 10,000 weight ppm.

[0024] Since the bisphenols for polymer raw materials of this invention can prevent that the polymer which was manufactured as a raw material and fabricated colors this as much as possible, it is transparent and it can be suitably used for it as manufacture raw materials, such as a polymer excellent in a hue, like there is no coloring, for example, the polycarbonate of an optical application, polyester, a polyether, and an epoxy resin.

[0025] As an approach of manufacturing the above-mentioned polycarbonate, polyester, a polyether, an epoxy resin, a polyether ether ketone, etc. using the bisphenols for polymer raw materials of this invention, a well-known approach is conventionally employable as it is.

[0026]

[Function] According to this invention, the phenolic compound in 4 used as a polymer raw material and 4'-bisphenols acts as a heat stabilizing agent at the time of manufacture of a polymer, and shaping, it is manufactured by this, and it is considered that that the fabricated polymer colors can prevent as much as possible.

[0027] Coloring of the polymer at the time of shaping originates in the heat deterioration of a polymer. As shown in a degree type, the phenolic compound (ArOH) which prevents this heat deterioration supplies a radical (R-) with a hydrogen atom from a polymer, serves as a stable phenoxy mold radical (ArO-) itself, and demonstrates the function in which a radical chain may be stopped by this.

$R\cdot + ArOH \rightarrow R-H + ArO\cdot$  and this stable phenoxy mold radical (ArO-) -- electron spin resonance (ESR) -- by observing by law, the function as a heat stabilizing agent of a phenolic compound can be checked. Therefore, the value of an ESR process and coloring of resin have large correlation.

[0028]

[Example] Hereafter, based on an example and the example of a comparison, this invention is explained concretely.

[0029] The acetone and the phenol were made to react by having made example 1 strongly acidic cation exchange resin into the catalyst, low-boiling point objects, such as water, were separated from the obtained reaction mixture, this was cooled, the adduct of bisphenol A and a phenol was deposited, the obtained adduct was separated, it recrystallized with the phenol and the refined crystal of adduct was obtained. This purification adduct (about 60 % of the weight of bisphenol A, about 40 % of the weight of phenols) was inserted in the film evaporator, the phenol was evaporated at a degree of vacuum 1.5 - 3Torr, and the temperature of 200 degrees C, and bisphenol A was obtained.

[0030] The class and concentration of the impurity of obtained bisphenol A were measured. For the result, it was residual phenol 10ppm, 2, 4-bisphenol A [general formula (2)] 24ppm, tris phenols [general formula (3)] 4ppm, 3-methylation bisphenol A [general formula (4)] 8ppm, and other 355 ppm, and the amount of sum total impurities was 401 ppm, and the sum total content of a general formula (2), (3), and (4) was 36 ppm.

[0031] Thus, 2 independently compounded to obtained bisphenol A and 4-bisphenol A [general formula (2)] 1000ppm were added, and bisphenol A for polymer raw materials whose sum total content of a general formula (2), (3), and (4) is 1036 ppm was manufactured.

[0032] Next, after carrying out the polymerization of this 22.3g of bisphenol A for polymer raw materials and 21.4g of diphenyl carbonate with scorification, reprecipitation purification was carried out with chloroform/methanol, and polycarbonate powder was manufactured. Existence of the stabilization radical which serves as an index of heat stabilization of resin about the obtained polycarbonate powder was measured by ESR.

[0033] After putting in and carrying out the nitrogen purge of the 0.15g of the polycarbonate powder to the quartz tube for ESR measurement (the bore of 3.75mm, outer diameter of 5.0mm), before this ESR measurement heated this, it was performed by the Measuring condition (magnetic field 323.5\*7.5mT, the magnetic field modulation frequency of 100kHz,

magnetic field modulation width-of-face 0.32mT, time constant 0.1 seconds of an amplifying circuit, the microwave output of 8mW, room temperature). The result was not able to observe an ESR signal. This shows before heating that there is no radical.

[0034] Next, after heating at 250-330 degrees C, it cooled and ESR measurement was performed like the above. The g value 2.0042 and the ESR signal of a stable phenoxy mold radical in which the single  $\Delta H_{pp}$  (peak-to-peak line width) 14.4G is shown were observed by the result.

[0035] Using bisphenol A which is 36 ppm, the sum total content of a general formula (2), (3), and (4) manufactured in the example of comparison 1 above-mentioned example 1 manufactured the polycarbonate like the example 1, and measured ESR before and behind heating like the example 1 about this polycarbonate. As for both results, an ESR signal was not observed before and after heating.

[0036] To 10g of bisphenol A whose sum total content of a general formula (2), (3), and (4) manufactured in the example 2 above-mentioned example 1 is 36 ppm 10g of bisphenol A whose sum total content of a general formula (2), (3), and (4) manufactured independently similarly is 1164 ppm was mixed to homogeneity, and 20g of bisphenol A for polymer raw materials whose sum total content of a general formula (2), (3), and (4) is 1200 ppm was manufactured.

[0037] After making it react in 1,2-dichloroethane using 10.8g of obtained bisphenol A for polymer raw materials, and 10.2g [ of mixture of terephthalic-acid chloride / isophthalic acid chloride 1:1 ], and p-tertiarybutyl phenol 0.76g, 11.1g [ of calcium hydroxides ], and triethylamine 0.1ml, reprecipitation purification was carried out and all aromatic polyester powder was manufactured.

[0038] Thus, about all the obtained aromatic polyester powder, ESR before and behind heating was measured like the above-mentioned example 1. Although an ESR signal was not observed before heating, the ESR signal was observed after heating by the result.

[0039] Using bisphenol A which is 36 ppm, the sum total content of a general formula (2), (3), and (4) manufactured in the example of comparison 2 above-mentioned example 1 manufactured all aromatic polyester powder like the example 2, and measured ESR before and behind heating like the above-mentioned example 1 about all these aromatic polyester powder. As for both results, an ESR signal was not observed before and after heating.

[0040]

[Effect of the Invention] In order for the bisphenols for polymer raw materials of this invention to manufacture transparent polymers, such as an optical application as which it can prevent that the polymer which is manufactured as a raw material and fabricated colors this as much as possible, and especially transparency and the hue of severe specification are required in it, it is useful as a raw material. Moreover, the approach of this invention is suitable as an approach of manufacturing such bisphenols for polymer raw materials.

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## EAST Search History

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## EAST Search History

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